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[Document Name] Specification 1

[Document Name] Abstract 1

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[Document Name] Specification

[Title of the Invention] PHOSPHOR AND METHOD OF PRODUCING SAME

[Scope of Claims for Patent]

[Claim 1] An alkaline earth metal aluminate phosphor
5 containing bivalent europium as an activator,
which contains at least one element selected from the
group consisting of indium, tungsten, niobium, bismuth,
molybdenum, tantalum, thallium and lead.

10 [Claim 2] The alkaline earth metal aluminate phosphor
according to Claim 1,
wherein the content of the at least one element selected
from the group consisting of indium, tungsten, niobium, bismuth,
molybdenum, tantalum, thallium and lead is within the range of
15 0.0001 to 0.01 mole per mole of the aluminum element.

[Claim 3] The alkaline earth metal aluminate phosphor
according to Claim 1 or 2,
wherein the alkaline earth metal aluminate phosphor
20 containing bivalent europium as an activator is represented by
the following general formula (1):
$$(Ba_{1-x}Sr_x)_{1-y}Eu_yMgAl_{10}O_{17} \quad (1)$$

in the formula, X satisfies the relationship of $0 \leq X \leq 0.3$ and
Y satisfies the relationship of $0 < Y \leq 0.2$.

25 [Claim 4] A method of producing alkaline earth metal aluminate
phosphors of any one of Claims 1 to 3,
which comprises a step of firing, in a reducing atmosphere,
a mixture of precursor compounds of barium and/or strontium(a),
30 magnesium(b), aluminum(c), europium(d) and at least one
element(e) selected from the group consisting of indium,
tungsten, niobium, bismuth, molybdenum, tantalum, thallium and
lead, respectively.

35 [Claim 5] The method according to Claim 4,

which further comprises a step of firing in an oxidizing atmosphere in advance of firing in a reducing atmosphere.

[Detailed Description of the Invention]

5 [0001]

[Technical Field of the Invention]

The present invention relates to an alkaline earth metal aluminate phosphor and a method of producing the same.

[0002]

10 [Background Art]

In recent years, various phosphors have been used in plasma display panels (hereinafter referred to as PDPs). Among such phosphors, alkaline earth metal aluminate phosphors containing bivalent europium as an activator, for example
15 (Ba,Sr)MgAl₁₀O₁₇:Eu²⁺, are used as blue phosphors.

[0003]

When exposed to elevated temperatures or to vacuum ultraviolet rays, ultraviolet rays or the like for phosphors excitation, such alkaline earth metal aluminate phosphors
20 containing bivalent europium as an activator deteriorate and decrease in luminance. The mechanism so far proposed as the cause therefor consists in the oxidation of bivalent Eu, which forms luminescence centers in the blue phosphors, in particular, to the trivalent form due to the oxidative effect of heating
25 on the phosphors surface, resulting in the loss of bivalent blue luminescence centers and the decrease in luminance.

[0004]

The phosphors may be subjected to heating at elevated temperatures in the step of molding for use in certain fields
30 of application. In the process of manufacturing PDPs, for instance, partitions called ribs are formed on the back face glass sheet, and the respective phosphors each in the form of a paste prepared by using a binder and a solvent are applied to respective partition-surrounded areas without color mixing.
35 The glass sheet is then heated at 400 to 500°C for binder

elimination in the manner of firing and for fusion bonding to a front face glass sheet. It is suggested that, in such a firing step, the firing is carried out in a high humidity environment as a result of not only the oxidative action but also the
5 evaporation of the moisture originally contained in dielectrics, electrodes and other materials than the phosphors, possibly affecting the fluorescent materials. Therefore, as far as blue phosphors are concerned, it is a great subject to inhibit luminance decreases as well as emission shifting in the
10 heating/firing step.

[0005]

For deterioration prevention, some attempts have already been made to prevent the deterioration by chemical treatment of the phosphors surface (e.g. Patent Document 1, Patent
15 Document 2, Patent Document 3). However, these methods consist in coating the surface with boric acid or a compound of such an element as antimony or silica and, therefore, it is difficult to entirely prevent the oxidative deterioration and, in addition, a problem arises, namely the luminance decreases due
20 to the covering of the phosphors surface with some other substance.

[0006]

[Patent Document 1] JP-10-195428 A

[Patent Document 2] JP-10-298548 A

25 [Patent Document 3] JP-10-204429 A

[0007]

[Problem to be solved by the Invention]

In view of the foregoing, it is an object of the present invention to provide an alkaline earth metal aluminate phosphor
30 having good heat resistance and durability against vacuum ultraviolet rays and ultraviolet rays, among others, and a method of producing the same.

[0008]

[Means for solving the Problem]

35 The present invention relates to an alkaline earth metal

aluminate phosphor containing bivalent europium as an activator,

which contains at least one element selected from the group consisting of indium, tungsten, niobium, bismuth, molybdenum, tantalum, thallium and lead.

[0009]

In the above-mentioned alkaline earth metal aluminate phosphor, the content of at least one element selected from the group consisting of indium, tungsten, niobium, bismuth, molybdenum, tantalum, thallium and lead is preferably within the range of 0.0001 to 0.01 mole per mole of the aluminum element.

[0010]

The above-mentioned alkaline earth metal aluminate phosphor containing bivalent europium as an activator is preferably represented by the following general formula (1):



in the formula, X satisfies the relationship of $0 \leq X \leq 0.3$ and Y satisfies the relationship of $0 < Y \leq 0.2$.

[0011]

The present invention also relates to a method of producing alkaline earth metal aluminate phosphors as mentioned above,

which comprises a step of firing, in a reducing atmosphere, a mixture of precursor compounds of barium and/or strontium(a), magnesium(b), aluminum(c), europium(d) and at least one element(e) selected from the group consisting of indium, tungsten, niobium, bismuth, molybdenum, tantalum, thallium and lead, respectively.

[0012]

Preferably, the above-mentioned method of producing alkaline earth metal aluminate phosphors comprises a step of firing in an oxidizing atmosphere in advance of firing in a reducing atmosphere.

In the following, the present invention is described in detail.

[0013]

The phosphors of the invention are an alkaline earth metal aluminate phosphor containing bivalent europium as an activator. Usable as the base phosphors are generally known ones, and there
5 may be mentioned, for example, alkaline earth metal aluminate phosphors comprising barium and/or strontium, europium, magnesium, aluminum and oxygen. Preferred as such alkaline earth metal aluminate phosphors are those represented by the following general formula (1):



in the formula, X satisfies the relationship of $0 \leq X \leq 0.3$ and Y satisfies the relationship of $0 < Y \leq 0.2$.

[0014]

The alkaline earth metal aluminate phosphor of the
15 invention is an alkaline earth metal aluminate phosphor containing bivalent europium as an activator and contains at least one element selected from the group consisting of indium, tungsten, niobium, bismuth, molybdenum, tantalum, thallium and lead. The element may occur either within the alkaline earth
20 metal aluminate phosphor or on the surface in a localized manner, such as resulting from surface treatment with a compound of that element. Preferably, however, it occurs within the alkaline earth metal aluminate phosphor. The phosphors may contain two or more metal species simultaneously or contain only one metal
25 species. Among the elements enumerated above, tungsten, niobium and bismuth are preferred, since they give phosphors having good heat resistance and durability against vacuum ultraviolet rays and ultraviolet rays, among others; and tungsten is most preferred.

30 [0015]

The content of the at least one element (e) selected from the group consisting of indium, tungsten, niobium, bismuth, molybdenum, tantalum, thallium and lead in the alkaline earth metal aluminate phosphor of the invention is preferably within
35 the range of 0.0001 to 0.01 mole per mole of the aluminum element.

At levels lower than 0.0001 mole, the effects of the addition will be little and, at levels exceeding 0.01 mole, the luminance will unfavorably become excessively low. The content level range differs depending on the element species employed. In
5 the case of tungsten and/or niobium, for instance, a preferred lower limit to the above range is 0.0003 mole, and a preferred upper range is 0.007 mole. Further, a most preferred lower limit to the above range is 0.0005 mole, and a most preferred upper limit is 0.003 mole. The content of the element can be
10 adjusted to a level within a specific range by adjusting the mixing ratio between the precursor compound of aluminum and the precursor compound of the above-mentioned element in the mixture of the precursor compounds used as the starting materials.

15 [0016]

The alkaline earth metal aluminate phosphor of the invention may further contain one or more elements other than the element at levels at which they will never adversely affect the physical properties of the phosphors. Since, however, the
20 presence of an impurity may influence the luminance, heat resistance, durability against vacuum ultraviolet ray and so forth, the content of elements other than the essential components should preferably be lower than 1%.

[0017]

25 In the following, alkaline earth metal aluminate phosphors of the invention is described referring to an example of methods of producing them. It is to be noted that the alkaline earth metal aluminate phosphor of the invention is not limited to the one produced by the production method described
30 below.

[0018]

The alkaline earth metal aluminate phosphor of the invention can be obtained by the step of firing, in a reducing atmosphere, a mixture of precursor compounds of the respective
35 elements (barium and/or strontium (a), magnesium (b), aluminum

(c), europium (d) and at least one element (e) selected from the group consisting of indium, tungsten, niobium, bismuth, molybdenum, tantalum, thallium and lead), which are the main constituents of the alkaline earth metal aluminate phosphor.

5 [0019]

The precursor compounds are not particularly restricted but each may be an oxide or any of compounds capable of being converted to oxides upon firing.

[0020]

10 The precursor compound of barium is not particularly restricted but includes, for example, barium oxide, barium carbonate, barium nitrate, barium sulfate, barium sulfide, barium chloride and barium hydroxide. The precursor compound of strontium is not particularly restricted but includes, for
15 example, strontium oxide, strontium carbonate, strontium nitrate, strontium sulfate, strontium sulfide, strontium chloride and strontium hydroxide. The precursor compound of magnesium is not particularly restricted but includes, for example, magnesium oxide, basic magnesium carbonate and
20 magnesium hydroxide. The precursor compound of aluminum is not particularly restricted but includes, for example, aluminum oxide, aluminum nitrate, aluminum sulfate and aluminum chloride. The precursor compound of europium is not particularly restricted but includes, for example, europium oxide, europium
25 carbonate, europium chloride and europium acetate. The oxidation number of the metal element is not particularly restricted, either.

[0021]

The precursor compound of indium is not particularly
30 restricted but includes, for example, indium oxide, indium trichloride, indium nitrate, indium hydroxide and indium sulfate. The oxidation number of the metal element is not particularly restricted, either. The precursor compound of tungsten is not particularly restricted but includes, for
35 example, tungsten oxide, ammonium tungstate and tungsten

hexachloride. The oxidation number of the metal element is not particularly restricted, either. The precursor compound of niobium is not particularly restricted but includes, for example, niobium oxide and niobium pentoxide. The oxidation number of the metal element is not particularly restricted, either. The precursor compound of bismuth is not particularly restricted but includes, for example, bismuth oxide and bismuth nitrate. The oxidation number of the metal element is not particularly restricted, either. The precursor compound of molybdenum is not particularly restricted but includes, for example, molybdenum oxide, ammonium molybdate and molybdenum chloride. The oxidation number of the metal element is not particularly restricted, either.

[0022]

The precursor compound of tantalum is not particularly restricted but includes, for example, tantalum oxide, tantalum chloride and tantalum fluoride. The oxidation number of the metal element is not particularly restricted, either. The precursor compound of thallium is not particularly restricted but includes, for example, thallium oxide, thallium carbonate and thallium nitrate. The oxidation number of the metal element is not particularly restricted, either. The precursor compound of lead is not particularly restricted but includes, for example, lead oxide, lead carbonate and lead nitrate. The oxidation number of the metal element is not particularly restricted, either.

[0023]

The compounds to be used as the precursor compounds each preferably has a purity as high as possible and, in particular, is preferably free of any impurity other than the volatile constituents or contains only a slight amount of such an impurity. If such an impurity is present in a starting material, the physical properties of the product alkaline earth metal aluminate phosphor may unfavorably be modified. It is preferable that each starting material have a purity of 99% or

higher. The above-mentioned respective precursor compounds are blended together, to give a mixture, in such proportions that they give the proportions of the respective elements in the alkaline earth metal aluminate phosphor to be produced.

5 [0024]

In producing the alkaline earth metal aluminate phosphor of the invention, a flux may further be used. The flux is not particularly restricted but is preferably one capable of functioning as a phosphors particle growth promoter and
10 volatilizing without influencing the composition of the phosphors, for example magnesium fluoride or aluminum fluoride.
[0025]

The mixture of the precursor compounds, if necessary further containing the flux, can be prepared mixing together
15 the respective components mentioned above by any of the conventional methods.

The method of mixing is not particularly restricted but may be any of those capable of causing homogeneous mixing without allowing aggregation of each individual component.
20 More specifically, there may be mentioned, for example, the dry mixing method using a ball mill or blender, for instance; the method comprising wet mixing in the presence of a solvent using a homogenizer or a like agitator, a ball mill, a bead mill or a like media grinder, followed by drying; the method comprising
25 preparing an aqueous solution of precursor compounds each in a water-soluble salt form, precipitating the precursor each in an insoluble salt form by pH adjustment with a pH adjusting agent so as to give a predetermined composition, washing the precipitate and drying the same; and the method comprising
30 preparing an aqueous solution of precursor compounds each in a water-soluble salt form, then preparing a W/O type emulsion using the solution and an oil, together with a dispersant, heating and dehydrating the emulsion and recovering the resulting oleaginous dispersion of the precursor mixture.

35 [0026]

The alkaline earth metal aluminate phosphor of the invention can be obtained by firing the above mixture in a reducing atmosphere. The firing is preferably carried out at a temperature within the range of 1000 to 1700°C. When the firing temperature is lower than 1000°C, the product alkaline earth metal aluminate phosphor may not occur as perfect crystals or, although the alkaline earth metal aluminate phosphor forms crystals, the crystallizability may markedly decline. Temperatures higher than 1700°C may give excessively large particles and cause marked deteriorations in performance characteristics, unfavorably making particle dispersion difficult due to strong intercrystalline fusion bonding and thus markedly inhibiting uniform fluorescent film formation. The above-mentioned firing is required to be carried out in a reducing atmosphere so that the fluorescence center europium may be reduced.

[0027]

Thus, the firing is carried out in a reducing atmosphere. The reducing atmosphere conditions are not particularly restricted but the firing is carried out, for example, in a nitrogen-hydrogen mixed gas atmosphere. In the firing in a nitrogen-hydrogen mixed gas atmosphere, the mixing ratio of nitrogen to hydrogen is preferably 99.9/0.1 to 80/20.

[0028]

The reaction time in the firing in a reducing atmosphere varies depending on the reaction temperature and, for the reaction to proceed satisfactorily, a reaction time of 0.5 to 10 hours, for instance, is employed, whereupon the desired alkaline earth metal aluminate phosphor can be obtained with great efficiency.

[0029]

In the above-mentioned method of producing alkaline earth metal aluminate phosphors, the firing in a reducing atmosphere may be preceded by an arbitrary number of firing steps each in an arbitrary atmosphere according to need. As such firing prior

to the firing in a reducing atmosphere, there may be mentioned, for example, the firing in an oxidizing atmosphere.

[0030]

The above-mentioned oxidizing atmosphere is not particularly restricted. There may be mentioned, for example, the firing in the ambient atmosphere or in a nitrogen-oxygen mixed gas atmosphere. The firing in an oxidizing atmosphere is preferably carried out at a temperature of 1000 to 1700°C. The reaction time in the firing in an oxidizing atmosphere varies depending on the reaction temperature; for the reaction to proceed satisfactorily, a reaction time of 0.5 to 10 hours, for instance, is employed, whereupon the intended purpose can be accomplished efficiently. In cases where the firing in a reducing atmosphere is carried out after the above-mentioned firing in an arbitrary atmosphere, the firing in a reducing atmosphere is preferably carried out after appropriate grinding of the fired product in an arbitrary atmosphere.

[0031]

The alkaline earth metal aluminate phosphor obtained by the method described above is preferably ground to adjust the particle diameter. Usable as the grinder to be used in the above-mentioned grinding are dry grinders such as hammer mills, fluid energy mills and mixing mullers, and wet grinders such as ball mills and bead mills. In the above-mentioned grinding, excessively intense grinding may result in marked deteriorations in phosphors characteristics and, therefore, it is necessary to select an adequate grinder or mill and employ best working conditions. The classification procedure using a liquid cyclone or the like may also be properly utilized.

[0032]

The alkaline earth metal aluminate phosphor of the invention as prepared above is excellent in heat resistance and in durability against vacuum ultraviolet rays or ultraviolet rays, and shows no luminance reduction, hence can be properly used in PDPs and in like applications. Furthermore, a method

for producing above alkaline earth metal aluminate phosphor constitutes one aspect of the present invention.

[0033]

5 The following examples further illustrate the present invention. They are, however, by no means limitative of the scope of the invention.

(Example 1)

10 Using an electronic force balance, 24.11 g of barium carbonate (purity on analysis: 99.39% by weight), 2.1 g of strontium carbonate (purity on analysis: 99.5% by weight), 8.33 g of magnesium hydroxide (purity on analysis: 99.5% by weight), 73.32 g of aluminum oxide (purity on analysis: 99.27% by weight), 1.26 g of europium(III) oxide (99.6% by weight), 0.166 g of tungsten(VI) oxide (special reagent grade) and 1.19 g of aluminum fluoride (special reagent grade) were weighed, and they were mixed up in an automatic mortar for 60 minutes. The mixture was then placed in an alumina crucible and fired in the ambient atmosphere by raising the temperature at a rate of 200°C per hour and, after arrival at the maximum temperature of 1500°C, maintaining that temperature for 5 hours, followed by temperature lowering at a rate of 200°C per hour. The thus-obtained fired product was ground in an automatic mortar for 10 minutes. Then, the fired product was subjected to reductive firing, in an electric oven maintained in a reducing atmosphere with a mixed gas composed of 10% by volume of hydrogen and 90% by volume of nitrogen, by raising the temperature at a rate of 200°C per hour and, after arrival at the maximum temperature of 1500°C, maintaining that temperature for 5 hours, followed by temperature lowering at a rate of 200°C per hour. The thus-obtained fired product was ground in an automatic mortar for 10 minutes. In the above manner, there was obtained an alkaline earth metal aluminate phosphor containing tungsten in an amount of 0.0005 mole as the element W per mole of aluminum.

35 [0034]

(Example 2)

An alkaline earth metal aluminate phosphor containing tungsten in an amount of 0.001 mole as the element W per mole of aluminum was obtained in the same manner as in Example 1 except that 0.331 g of tungsten(VI) oxide (special reagent grade) was added in lieu of the addition of 0.166 g of tungsten(VI) oxide (special reagent grade).

[0035]

(Comparative Example 1)

An alkaline earth metal aluminate phosphor was obtained in the same manner as in Example 1 except that the addition of 0.166 g of tungsten(VI) oxide (special reagent grade) was omitted.

[0036]

(Heat resistance testing method)

Two grams of each of the phosphors prepared in Examples 1 and 2 and Comparative Example 1 was weighed in a porcelain crucible and fired in an electric oven in the air by raising the temperature at a rate of 200°C per hour and, after arrival at the temperature of 500°C, maintaining that temperature for 1 hour, followed by temperature lowering at a rate of 200°C per hour. Separately, firing was carried out in the same manner except that the temperature maintenance was at 600°C, 700°C, 800°C or 900°C. Using an Otsuka Electronics model MCPD-3000 fluorescence spectrophotometer, the values of luminance of each of the phosphors of Examples 1 and 2 and Comparative Example 1 before and after the oxidizing firing were determined. The percent luminance retentions were calculated according to the formula (luminance after firing)/(luminance before firing) x 100, and the respective samples were compared with one another with respect to deterioration resistance in terms of the percent luminance retention after firing as compared with the luminance before firing. The results are shown in Table 1.

[0037]

35

Table 1

	Tungsten element content	Luminance retention (%)				
		500°C	600°C	700°C	800°C	900°C
Example1	0.0005	97.8	94.8	89.6	88.0	83.0
Example2	0.001	100.2	96.4	90.8	89.1	82.2
Comparative Example1	-	98.4	91.9	86.6	84.3	78.6

[0038]

As is evident from the data shown in Table 1, the alkaline
5 earth metal aluminate phosphors obtained in Examples 1 and 2
with tungsten added are both higher in luminance retention
percentage after firing, hence improved in resistance to
oxidation-due deterioration, as compared with the
tungsten-free alkaline earth metal aluminate phosphor obtained
10 in Comparative Example 1.

[0039]

(Example 3)

Using an electronic force balance, 22.69 g of barium
carbonate (purity on analysis: 99.39% by weight), 2.14 g of
15 strontium carbonate (purity on analysis: 99.5% by weight), 8.33
g of magnesium hydroxide (purity on analysis: 99.5% by weight),
72.96 g of aluminum oxide (purity on analysis: 99.27% by weight),
2.52 g of europium(III) oxide (99.6% by weight), 0.197 g of
indium(III) oxide and 1.20 g of aluminum fluoride (special
20 reagent grade) were weighed, and they were mixed up in an
automatic mortar for 60 minutes. The mixture was then placed
in an alumina crucible and fired in the ambient atmosphere by
raising the temperature at a rate of 200°C per hour and, after
arrival at the maximum temperature of 1500°C, maintaining that
25 temperature for 5 hours, followed by temperature lowering at
a rate of 200°C per hour. The thus-obtained fired product was
ground in an automatic mortar for 10 minutes. Then, the fired
product was subjected to reductive firing, in an electric oven

maintained in a reducing atmosphere with a mixed gas composed of 10% by volume of hydrogen and 90% by volume of nitrogen, by raising the temperature at a rate of 200°C per hour and, after arrival at the maximum temperature of 1500°C, maintaining that
5 temperature for 5 hours, followed by temperature lowering at a rate of 200°C per hour. The thus-obtained fired product was ground in an automatic mortar for 10 minutes.

In the above manner, there was obtained an alkaline earth metal aluminate phosphor containing indium in an amount of 0.001
10 mole as the element In per mole of aluminum.

[0040]

(Example 4)

An alkaline earth metal aluminate phosphor containing tungsten in an amount of 0.001 mole as the element W per mole
15 of aluminum was obtained in the same manner as in Example 3 except that 0.329 g of tungsten(VI) oxide (special reagent grade) was added in lieu of the addition of 0.197 g of indium(III) oxide.

[0041]

(Example 5)

20 An alkaline earth metal aluminate phosphor containing tungsten in an amount of 0.002 mole as the element W per mole of aluminum was obtained in the same manner as in Example 3 except that 0.658 g of tungsten(VI) oxide (special reagent grade) was added in lieu of the addition of 0.197 g of indium(III) oxide.

25 [0042]

(Example 6)

An alkaline earth metal aluminate phosphor containing tungsten in an amount of 0.005 mole as the element W per mole of aluminum was obtained in the same manner as in Example 3 except
30 that 1.66 g of tungsten(VI) oxide (special reagent grade) was added in lieu of the addition of 0.197 g of indium(III) oxide.

[0043]

(Example 7)

An alkaline earth metal aluminate phosphor containing
35 niobium in an amount of 0.001 mole as the element Nb per mole

of aluminum was obtained in the same manner as in Example 3 except that 0.189 g of niobium(V) pentoxide was added in lieu of the addition of 0.197 g of indium(III) oxide.

[0044]

5 (Example 8)

An alkaline earth metal aluminate phosphor containing niobium in an amount of 0.002 mole as the element Nb per mole of aluminum was obtained in the same manner as in Example 3 except that 0.378 g of niobium(V) pentoxide was added in lieu of the
10 addition of 0.197 g of indium(III) oxide.

[0045]

(Example 9)

An alkaline earth metal aluminate phosphor containing bismuth in an amount of 0.001 mole as the element Bi per mole
15 of aluminum was obtained in the same manner as in Example 3 except that 0.331 g of bismuth(III) oxide was added in lieu of the addition of 0.197 g of indium(III) oxide.

[0046]

(Example 10)

20 An alkaline earth metal aluminate phosphor containing molybdenum in an amount of 0.001 mole as the element Mo per mole of aluminum was obtained in the same manner as in Example 3 except that 0.205 g of molybdenum(VI) oxide was added in lieu of the addition of 0.197 g of indium(III) oxide.

25 [0047]

(Example 11)

An alkaline earth metal aluminate phosphor containing tantalum in an amount of 0.001 mole as the element Ta per mole of aluminum was obtained in the same manner as in Example 3 except
30 that 0.314 g of tantalum(V) oxide was added in lieu of the addition of 0.197 g of indium(III) oxide.

[0048]

(Example 12)

35 An alkaline earth metal aluminate phosphor containing thallium in an amount of 0.001 mole as the element Tl per mole

of aluminum was obtained in the same manner as in Example 3 except that 0.324 g of thallium(III) oxide was added in lieu of the addition of 0.197 g of indium(III) oxide.

[0049]

5 (Example 13)

An alkaline earth metal aluminate phosphor containing lead in an amount of 0.001 mole as the element Pb per mole of aluminum was obtained in the same manner as in Example 3 except that 0.317 g of lead(II) oxide was added in lieu of the addition
10 of 0.197 g of indium(III) oxide.

[0050]

(Comparative Example 2)

An alkaline earth metal aluminate phosphor was obtained in the same manner as in Example 3 except that the addition of
15 0.197 g of indium(III) oxide was omitted.

[0051]

(Heat resistance testing method)

The phosphors prepared in Examples 3 to 13 and Comparative Example 2 were subjected to deterioration resistance evaluation
20 at the predetermined maximum temperature of 900°C in the same manner as in the heat resistance testing with the products of Examples 1 and 2 and Comparative Example 1, and the deterioration resistance features of the samples before and after firing were compared in terms of luminance retention
25 percentage. The results are shown in Table 2.

[0052]

Table 2

	Element species	Element content	Luminance retention(%)
Example3	In	0.001	82.6
Example4	W	0.001	97.5
Example5	W	0.002	96.2
Example6	W	0.005	85.4
Example7	Nb	0.001	83.0
Example8	Nb	0.002	90.4
Example9	Bi	0.001	87.0
Example10	Mo	0.001	82.3
Example11	Ta	0.001	83.1
Example12	Tl	0.001	84.7
Example13	Pb	0.001	82.5
Comparative Example2	—	—	79.0

[0053]

As is evident from the results shown in Table 2, the alkaline earth metal aluminate phosphors obtained in Examples 3 to 13 all showed improved luminance retention percentages after firing, hence were improved in deterioration resistance, as compared with the alkaline earth metal aluminate phosphor of Comparative Example 2.

10 [0054]

(Example 14)

An alkaline earth metal aluminate phosphor containing tungsten in an amount of 0.0005 mole as the element W per mole of aluminum was obtained in the same manner as in Example 3 except that 0.166 g of tungsten(VI) oxide (special reagent grade) was added in lieu of the addition of 0.197 g of indium(III) oxide.

[0055]

(Example 15)

An alkaline earth metal aluminate phosphor containing niobium in an amount of 0.0005 mole as the element Nb per mole of aluminum was obtained in the same manner as in Example 3 except that 0.095 g of niobium(V) pentoxide was added in lieu of the

addition of 0.197 g of indium(III) oxide.

[0056]

(Deterioration testing by vacuum ultraviolet irradiation)

The alkaline earth metal aluminate phosphors obtained in
5 Examples 4, 14 and 15 and Comparative Example 2 were subjected
to testing for deterioration with the passage of time under
vacuum ultraviolet irradiation. In carrying out the test, test
films to be irradiated with vacuum ultraviolet rays were first
prepared. Thus, each of the alkaline earth metal aluminate
10 phosphors obtained in the examples and comparative example was
mixed with ethylcellulose and terpeneol in a ratio of 17.5:1:9
on the weight basis, and the mixture was dispersed on a Hoover
muller to give a phosphors paste. Each phosphors paste was
applied onto a slide glass to give a 2 x 2 cm square film with
15 a dry film thickness of 20 μm , and the film was fired in the
air at 500°C for 20 minutes to remove the binder and solvent
components.

[0057]

The thus-obtained fired films were used as test specimens.
20 Each test specimen was irradiated with ultraviolet rays at 147
nm under vacuum (≤ 5 Pa) for 2 hours using a vacuum ultraviolet
lamp (product of Ushio Inc.). The luminance after irradiation
was measured, and the luminance retention percentage, i.e.
(luminance after irradiation/luminance before irradiation) x
25 100, was calculated. Based on the luminance retention data thus
obtained, the extents of deterioration of the test specimens
before and after irradiation were compared with one another.
The results are shown in Table 3.

[0058]

30

Table 3

	Element species	Element content	Luminance retention(%)
Example4	W	0.001	92
Example14	W	0.0005	90
Example15	Nb	0.0005	95
Comparative Example2	-	-	85

[0059]

As is evident from the results shown in Table 3, the
5 alkaline earth metal aluminate phosphors produced in Examples
4, 14 and 15 according to the invention showed improved
luminance retention percentages higher by 5 to 10% as compared
with the alkaline earth metal aluminate phosphor of Comparative
Example 2. Thus, the present invention produces not only the
10 effect of inhibiting deterioration due to oxidation but also
the effect of preventing the progress of deterioration due to
vacuum ultraviolet rays.

[0060]

[Effect of the Invention]

15 It is apparent that the alkaline earth metal aluminate
phosphor of the invention is a phosphors excellent in luminance
retention performance with the deterioration with time upon
heating and vacuum ultraviolet irradiation being markedly
suppressed.

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[Document Name] Abstract

[Abstract]

[Subject] To provide an alkaline earth metal aluminate
phosphor having good heat resistance and durability against
5 vacuum ultraviolet rays and ultraviolet rays, among others, and
a method of producing the same.

[Means for solving] An alkaline earth metal aluminate phosphor
containing bivalent europium as an activator, which contains
at least one element selected from the group consisting of
10 indium, tungsten, niobium, bismuth, molybdenum, tantalum,
thallium and lead.

[Selective Figure] None